

TEST EVALUATION OF FUEL CELL CATALYSTS

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## I. SUMMARY

During the second quarter of the contract, the second group of compounds supplied by the U. S. Bureau of Mines was tested for catalytic activity in the oxidation of  $N_2H_4$ . Some compounds showed very high activity in the oxidation of  $N_2H_4$ , although all compounds corroded in the test electrolyte solution.

Selected catalysts from the first group were further examined for their characteristics on the  $N_2H_4$  anode. The most interesting result was the extremely high  $NH_3$  content in the gas evolved from these electrodes.

## II. INTRODUCTION

The objective of this contract is to determine certain essential properties of non-noble metal compounds as electrode catalysts for fuel cells. Properties of major interest include: polarization characteristics of the electrodes containing these compounds; and the chemical stability of these electrodes in prescribed test environments.

The work undertaken at Monsanto Research Corporation is to investigate the electrocatalytic activity of the compounds for oxidation of dextrose and hydrazine.

During the first quarter, interstitial compounds, namely, carbide, nitride, carbonitride and nitrocarbide of iron were investigated. Results showed that no compounds were catalytically active for dextrose oxidation in buffered neutral electrolyte, but all compounds were sufficiently active for  $N_2H_4$  oxidation in KOH electrolyte. Some compounds, particularly those prepared from leached Raney iron, however, showed significantly severe corrosion in the caustic electrolyte.

During this quarter, leached Raney alloys of Ni, Co and Ag, and their carbides and nitrocarbides were supplied by the U. S. Bureau of Mines. These were evaluated in the same manner as the first group of catalysts. Some additional experiments on some of the promising catalysts from the first group were also conducted.

### III. PREPARATION OF ELECTRODES

All catalysts were preconditioned according to the procedure described in the first quarterly report.

Since one catalyst of the first group ignited during grinding, all catalysts of the second group were ground and sieved to -400 mesh in a chemically pure argon atmosphere prior to the final preconditioning process.

All electrodes prepared during the second quarter were type B\*. These electrodes contain a network of macropores in a micro-porous matrix and are considered very suitable for the present study.

Catalyst loading was approximately 0.7g/inch<sup>2</sup>.

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\* *The method for preparing this type electrode is Monsanto Research proprietary.*

## IV. TEST RESULTS

### A. CORROSION TESTING

Weighed samples (about 0.5 gram each) were soaked overnight in 50 cc of 5M KOH in a constant temperature bath at 70°C. The following day, they were collected by filtration, dried in vacuum, and weighed. All samples were found to have gained weight, perhaps due to formation of hydroxide or hydrated oxides on the surface of the powder. The samples containing cobalt formed a blue color in the test solution. The same tests were run in 5M KOH with 2M N<sub>2</sub>H<sub>4</sub> added. However, the gas evolution produced by decomposition of hydrazine was so vigorous that portions of the samples were lost. Therefore, weighing after the corrosion tests was omitted. Coloring of the solutions was somewhat different from that in KOH without N<sub>2</sub>H<sub>4</sub>.

Finally, the samples were tested in inhibited 0.1M HCl. In all cases, there was significant loss of weight. Most of the leached Raney alloys produced gas evolution as well.

Results are summarized in Table 1.

### B. DEXTROSE OXIDATION

Evaluation of catalytic activity for dextrose oxidation was to be carried out under contract PH43-66-976, "Implantable Fuel Cell for an Artificial Heart", for the National Heart Institute, Department of Health, Education and Welfare.

Since contamination of the blood system due to corrosion of electrode material is impermissible, we determined that these catalysts are not appropriate for this application. Consequently, no experiments were carried out for this phase.

### C. N<sub>2</sub>H<sub>4</sub> OXIDATION

Although the corrosion tests revealed that most of the catalysts in the second group were attacked in some degree by the test electrolyte (5M KOH + 2M N<sub>2</sub>H<sub>4</sub>), the polarization data for N<sub>2</sub>H<sub>4</sub> oxidation was taken in the manner described in the previous report.

IR free electrode potentials vs the saturated calomel electrode at various current densities above 10 mA/cm<sup>2</sup> (apparent densities) are given in Table 2. Results indicate that some catalysts are very active in N<sub>2</sub>H<sub>4</sub> oxidation. Eight catalysts were selected from the first group (interstitial compounds of

Table 1

## CORROSION TESTS

Catalyst	Effect of 5M KOH		Effect of 0.1M HCl		Effect of 5M KOH 2M N <sub>2</sub> H <sub>4</sub>	
	Color	Wt. Gain, %	Color	Wt. Loss, %	Color	Weight
33C Co-C	Blue	8	None	7	None	samples
35C Ni-C	None	15	None	6	None	not
38C 1Co:3Ag-C	Pale blue	5	None	21	Blue	weighed
39C 1Co:1Ag-C	Pale blue	22	None	10	Yellow	after test
42C 1Ni:1Co-C	Pale blue	22	None	7	Yellow	due to loss
43C 1Ni:1Ag-C	None	13	None	10	Yellow	by excessive
46C 3Ni:1Ag-C	Pale yellow	17	None	19	None	gassing of
21NC Co-NC	Blue	29	None	14	Yellow	the N <sub>2</sub> H <sub>4</sub>
23NC Ni-NC	None	30	None	18	None	
28NC 1Ni:1Co-NC	Blue	21	None	23	None	
31NC 1Ni:1Ag-NC	Pale yellow	2	None	27	Yellow	
32NC 3Ni:1Ag-NC	None	12	None	11	None	
RAL2 1Ni:1Co-RAL	Blue	18	Pink, gas evolved	27	Yellow	
RAL3 3Ni:1Co-RAL	Pale blue	29	None	21	Yellow	
RAL4 1Ni:3Ag-RAL	None	17	None	23	Yellow	
RAL5 1Ni:1Ag-RAL	None	27	None	22	None	
RAL6 3Ni:1Ag-RAL	Pale yellow	20	None	26	None	
RAL7 1Co:3Ag-RAL	Blue	13	pink, gas evolved	33	Blue	
RAL8 1Co:1Ag-RAL	Pale blue	16	pink, gas evolved	28	None	
RAL9 3Co:1Ag-RAL	Pale blue	11	pink, gas evolved	33	None	
RAL10 1Ni:1Co:1Ag-RAL	Pale blue	25	None	23	Yellow	
RAL11 1Ni:1Co:1Au-RAL	Pale blue	41	None, rapid gas evolved	26	None	
RAL12 1Ni:1Ag:1Au-RAL	Pale yellow	11	Green, rapid gas evolved	28	Yellow	
RAL13 1Co:1Ag:1Au-RAL	Blue	4	Pink, gas evolved	25	None	
RC1 Co-RC	Blue	20	Pink, gas evolved	13	None	
RN2 Ni-RN	None	29	Green, no gas	20	Yellow	

C = carbide; NC = Nitrocarbide; RAL, RC, RN = leached Raney alloy

Table 2

POTENTIAL OF VARIOUS  $N_2H_4$  ELECTRODE

vs.

THE SATURATED CALOMEL ELECTRODE  
AT VARIOUS CURRENT DENSITIES (IR FREE)

Electrode: B Type

Electrolyte: 5M KOH + 2M  $N_2H_4$ 

Temperature: 70°C

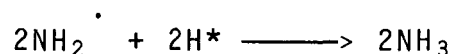
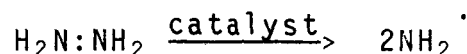
		<u>Current Densities, mA/cm<sup>2</sup></u>				
<u>Catalysts</u>		<u>OCP</u>	<u>10</u>	<u>20</u>	<u>50</u>	<u>100</u>
33C	Co-C	-1.22	-1.22	-1.21	-1.21	-1.19
35C	Ni-C	-1.19	-1.18	-1.16	-1.14	-1.12
38C	1Co:3Ag-C	-1.17	-1.16	-1.16	-1.15	-1.09
39C	1Co:1Ag-C	-1.22	-1.22	-1.22	-1.21	-1.21
42C	1Ni:1Co-C					
43C	1Ni:1Ag-C	-1.21	-1.21	-1.19	-1.19	-1.19
46C	3Ni:1Ag-C	-1.23	-1.21	-1.20	-1.18	-1.18
21NC	Co-NC	-1.23	-1.23	-1.20	-1.20	-1.19
23NC	Ni-NC	-1.16	-1.13	-1.10	-1.09	-1.07
28NC	1Ni:1Co-NC	-1.16	-1.11	-1.09	-1.03	-0.85
31NC	1Ni:1Ag-NC	-1.25	-1.25	-1.25	-1.21	-1.21
32NC	3Ni:1Ag-NC	-1.19	-1.13	-1.12	-1.12	-1.12
RAL2	1Ni:1Co-RAL	-1.12	-1.12	-1.10	-1.10	-1.05
RAL3	3Ni:1Co-RAL	-1.25	-1.25	-1.25	-1.23	-1.23
RAL4	1Ni:3Ag-RAL	-1.20	-1.19	-1.19	-1.14	-1.12
RAL5	1Ni:1Ag-RAL	-1.15	-1.15	-1.12	-1.12	-1.12
RAL6	3Ni:1Ag-RAL	-1.15	-1.15	-1.15	-1.13	-1.10
RAL7	1Co:3Ag-RAL	-1.24	-1.23	-1.22	-1.20	-1.16
RAL8	1Co:1Ag-RAL	-1.23	-1.23	-1.20	-1.18	-1.17
RAL9	3Co:1Ag-RAL	-1.25	-1.25	-1.25	-1.25	-1.25
RAL10	1Ni:1Co:1Ag-RAL	-1.23	-1.23	-1.23	-1.20	-1.20
RAL11	1Ni:1Co:1Au-RAL	-1.23	-1.23	-1.23	-1.23	-1.23
RAL12	1Ni:1Ag:1Au-RAL	-1.20	-1.19	-1.19	-1.19	-1.18
RAL13	1Co:1Ag:1Au-RAL	-1.24	-1.23	-1.23	-1.22	-1.22
RC1	Co-RC	-1.25	-1.25	-1.25	-1.24	-1.19
RN2	Ni-RN	-1.16	-1.16	-1.16	-1.15	-1.15

C = carbide; NC = nitrocarbide; RAL, RC, RN = leached Raney metal  
or alloy



iron) for further investigation. They were made into 2 x 2 inch B type electrodes having catalyst loadings of approximately 0.7 g/in.<sup>2</sup>. The rate of gas evolution, composition of the evolved gas and electrode potentials for these electrodes were determined at open circuit and under polarization at 100 amp/ft<sup>2</sup>. These data are specifically important in the practical operation of N<sub>2</sub>H<sub>4</sub>-Air fuel cell systems.

Data are summarized in Table 3. The most interesting result from the data is the extremely high content of NH<sub>3</sub> in the evolved gas. It is about 100 to 1000 times higher than the average NH<sub>3</sub> content from the presently operating MRC N<sub>2</sub>H<sub>4</sub>-electrode. At present we do not have an established mechanism for NH<sub>3</sub> formation on the N<sub>2</sub>H<sub>4</sub> anode. However, we suggest that these high NH<sub>3</sub> contents may be due to unusually high activity of these compounds for breaking N<sub>2</sub> bonding, as shown in the following equation:



where 2H\* are products of the local cathodic reaction on the N<sub>2</sub>H<sub>4</sub> anode.

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